

French Republic  
□  
MINISTRY OF INDUSTRY  
Patent Service

**PATENT**

File No. 968,281

No. 1,399,615

Int. Cl.: A01n - C07c - C07d

**New chemical compounds and herbicidal composition containing them**

CHEMICAL INVESTORS S.A., Luxemburg

Applied for on March 23, 1964

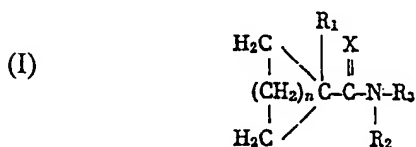
Issued by decree of April 12, 1965

(Official Patent Bulletin No. 21, 1965)

(Two patent applications filed in the United States of America on March 28, 1963, No. 268,581 in the name of Thomas Robert Hopkins and on May 8, 1963, No. 278,974 in the name of Kenneth Paul Dubrovin)

The invention has as its subject new chemical compounds, herbicidal compositions containing them as the active ingredient, and procedures aimed at preventing the growth of plants using these compositions.

The new chemical compounds according to the invention correspond to the formula:



in which:

N is 0 or 1;

R<sub>1</sub> is an alkyl, haloalkyl, alkoxy, aryl group or a halogen atom;

R<sub>2</sub> and R<sub>3</sub> are, independently, hydrogen atoms or alkyl, cycloalkyl, alkenyl, alkynyl, aralkyl, aryl, alkaryl, haloaryl, or haloalkaryl groups or heterocyclic groups, but can also together form a heterocyclic radical with the nitrogen atom to which they are attached; X is an atom of oxygen or sulfur.

To simplify the description, these compounds will hereinafter be called "cycloalkanecarboxamides." As can be seen, the invention compounds are either unsubstituted amides, or amides bearing one or more organic substituents on the nitrogen atom.

The above cycloalkanecarboxamides can be mixed with inert vehicles or emulsifiers, etc. to form herbicidal compositions that can serve efficaciously to prevent the growth of plants. The herbicidal compositions obtained can act before or after emergence from the ground.

The following examples are given to illustrate more clearly the principle and practice of the invention.

*Examples 1 to 4.* For the preparation of four amides of 1-methylcyclopropanecarboxylic acid, methyl 1-methylcyclopropanecarboxylate is caused to react with 3-chloroaniline, 3-chloro-4-methylaniline, 2-methyl-5-chloroaniline and 3,4-dichloroaniline, respectively.

In each synthesis, 0.1 mole methyl 1-methylcyclopropanecarboxylate, 0.1 mole of the amine, 0.11 mole sodium methoxide and 200 cm<sup>3</sup> benzene are stirred and heated under gentle reflux. The refluxing is continued for about twelve hours while eliminating the benzene-methanol azeotrope as it is formed. The reaction mixture is cooled to ambient temperature, then 50 cm<sup>3</sup> water and 15 cm<sup>3</sup> concentrated hydrochloric acid dissolved in 40 cm<sup>3</sup> water are added. After being mixed well, the organic phase is recovered by decantation and it is extracted successively with dilute hydrochloric acid and with water. The organic phase is dried, and decolorized with charcoal. After elimination of the benzene under reduced pressure, the amides obtained are recrystallized from ligroin. The identification of the amides prepared (Examples 1, 2, 3 and 4) and their melting points are indicated in Table I.

Three amides of 1-methylcyclopropanecarboxylic acid are preferably prepared by a variant in which 1-methylcyclopropanecarbonyl chloride is caused to react with 2,6-dichloroaniline, 2,6-dimethylaniline and 2,5-dimethylaniline, respectively. The acyl chloride is advantageously prepared by causing a solution of 7.8 g (0.078 mole) 1-methylcyclopropanecarboxylic acid to react with 20 cm<sup>3</sup> thionyl chloride in a state of repose for sixteen hours, then eliminating the excess thionyl chloride by distillation under reduced pressure. The residue is made up mainly of 1-methylcyclopropanecarbonyl chloride (b.p. 132-134°C at 760 mm Hg); it is then caused to react with the

substituted aniline compound without further purification by the procedure explained in Section D of Example 7, below, or by other procedures known to one skilled in the art. The identification of the amides prepared (Examples 4, 5 and 5a) and their melting points are indicated in table I.

Table I

Exemple	Amide	Point de fusion °C
I.....	N-(3-chlorophényl)-1-méthyl-cyclopropane-1-carboxamide.	118-120
II.....	N-(3-chloro-4-méthylphényl)-1-méthylcyclopropane-1-carboxamide.	103-105
III.....	N-(2-méthyl-5-chlorophényl)-1-méthylcyclopropane-1-carboxamide.	79-81
IV.....	N-(2,6-dichlorophényl)-1-méthylcyclopropane-1-carboxamide.	147-149
V.....	N-(2,6-diméthylphényl)-1-méthylcyclopropane-1-carboxamide.	128-130
Va.....	N-(2,5-diméthylphényl)-1-méthylcyclopropane-1-carboxamide.	84-85
VI.....	N-(3,4-dichlorophényl)-1-méthylcyclopropane-1-carboxamide.	89-91

#### KEY TO TABLE

Point de fusion = Melting point

#### Example 7:

Section A. A solution of 20.1 g (0.3 mole) cyclopropanecarbonitrile, 45.2 g (0.33 mole) freshly distilled butyl bromide and 500 cm<sup>3</sup> benzene is heated at 76°C. A slurry of sodamide in benzene (freshly prepared from 6.9 g or 0.3 gram-atom sodium in 150 cm<sup>3</sup> benzene) is added slowly to this so as to maintain the reflux, and external heating is discontinued. Once the addition of sodamide is finished, external heat is again applied and the mixture is heated under reflux for twenty-four hours. To the mixture is then added an additional 12 g butyl bromide and the refluxing is continued for a further twenty-four hours. The mixture is then cooled, successively extracted with water, dilute phosphoric acid, and a new portion of water, and finally it is dried. The benzene is evaporated off by distillation under reduced pressure and the product is distilled under vacuum to obtain 9.5 g liquid which boils at 68-70°C under 7 mm Hg and has a refractive index of 1.4326 at 19°C. The product is 1-butylcyclopropanecarbonitrile.

Section B. A mixture of 13 g (0.106 mole) 1-butylcyclopropanecarbonitrile and 34 g (0.26 mole) 75% sulfuric acid is stirred and heated to 130-135°C for one hour. The solution is then cooled and held below 60°C while adding in small portions 14.6 g (0.212 mole) sodium nitrile to facilitate the hydrolysis of the nitrile group. Once the addition of sodium nitrile is finished,

the mixture is stirred at ambient temperature for one hour then poured on to ice. The organic phase is taken up in a little ether and dried. After elimination of the ether, the material is distilled to obtain 1-butylcyclopropanecarboxylic acid which has a boiling point of 89-94°C under 1 mm Hg, and a refractive index of 1.4496 at 19°C.

Section C. A solution of 11 g (0.078 mole) 1-butylcyclopropanecarboxylic acid and 20 cm<sup>3</sup> thionyl chloride is left to stand for sixteen hours at 25°C, then heated under reflux for two hours. The excess thionyl chloride is removed under reduced pressure and the residue is distilled under vacuum to obtain 9.7 g 1-butylcyclopropanecarbonyl chloride which has a boiling point of 67-69°C under 10 mm Hg.

Section D. The acyl chloride prepared as in Section C is added slowly to a stirred solution containing 9.8 g (0.064 mole) 3,4-dichloroaniline, 5.06 g (0.064 mole) pyridine and 100 cm<sup>3</sup> benzene. Then 100 cm<sup>3</sup> ethyl acetate is added and the reaction mixture is heated under reflux for two hours. The mixture is cooled and extracted successively with water, dilute hydrochloric acid, water, a dilute solution of sodium bicarbonate, and water. The organic solution is then dried and decolorized over charcoal. The solvents are eliminated under reduced pressure then the residue is recrystallized from heptane to obtain 15.1 g product which melts at 118.5-120°C. The product is N-(3,4-dichlorophenyl)-1-butylcyclopropanecarboxamide.

Examples 7 to 13. A series of amides is prepared by causing 1-chlorocyclopropanecarbonyl chloride (obtained by the method of Bruylanta, Acad. Royale de Belgique, Bulletin 705 (1921)) to react with p-phenylazoaniline, p-acetylaniline, 3,4-dichloroaniline, 3-chloroaniline, and 3-chloro-4-methylaniline, respectively, by the method in Example 7, section D. The amides prepared and their melting points are indicated in table II.

(See Table II, page 3)

Example 14. 1-Bromocyclobutanecarbonyl chloride is prepared by the method of Campbell and Raydon (J. Chem. Soc., 3002 (1953)). This substance is caused to react with 3,4-dichloroaniline by the method described in Example 7, Section D, to obtain N-(3,4-dichlorophenyl)-1-bromocyclobutanecarboxamide, which melts at 96-97°C.

Table II

Exemple	Amide	Point de fusion °C
VIII.....	N-p-(phénylazo)phényl-1-chlorocyclopropanecarboxamide.	196-198
IX.....	N-(p-acétylphényl)-1-chlorocyclopropanecarboxamide.	183-185
X.....	N-phényl-1-chlorocyclopropanecarboxamide.	62-63
XI.....	N-(3,4-chlorophényl)-1-chlorocyclopropanecarboxamide.	95-96
XII.....	N-(3-chlorophényl)-1-chlorocyclopropanecarboxamide.	73-74
XIII.....	N-(3-chloro-4-méthylphényl)-1-chlorocyclopropanecarboxamide.	89-90

**KEY TO TABLE:**

Point de fusion = Melting point

*Example 15.* N-Phenyl-1-bromocyclobutanecarboxamide is prepared by causing 1-bromocyclobutanecarbonyl chloride to react with aniline by the method described in Example 14. The compound melts at 89-90°C.

*Example 16.* N-Phenyl-1-phenylcyclopropanecarboxamide is prepared by causing 1-phenylcyclopropanecarbonyl chloride to react with aniline by the method described in Example 14. The compound melts at 123-125°C.

*Example 17. a.* Preparation of 4-chloro-2-methoxybutyronitrile.

This compound is prepared by a procedure similar to that used by Wilson and Henze, J. Am. Chem. Soc. 63, 2112 (1941), to prepare 4-chloro-1-ethoxy-butyronitrile.

To 147 g (1.1 mole) silver cyanide dispersed in 300 cm<sup>3</sup> anhydrous ether is added a solution of 140 g (0.98 mole) 1,3-dichloro-1-methoxypropane in 250 cm<sup>3</sup> anhydrous ether. A gentle reflux is produced during the addition. Once the addition is finished, the slurry is stirred overnight at ambient temperature. The mixture is then filtered and the ether is removed by distillation. The residue is then distilled to obtain 78.1 g product boiling at 67-69°C under a pressure of 8 mm Hg;  $n_D^{17}$  1.4339.

*b.* Preparation of methyl 4-chloro-2-methoxybutyrate

A solution of 40 g (0.3 mole) 4-chloro-2-methoxybutyronitrile in 80 cm<sup>3</sup> methanol is saturated with hydrochloric acid at ambient temperature then heated under reflux for sixteen hours. The mixture is poured into 150 cm<sup>3</sup> cold water, the organic layer is separated and the aqueous layer is extracted with three small portions of ether to recover an additional amount of product from the aqueous phase. The organic phases are combined, dried, then distilled to obtain 37 g product boiling at 93-96°C under 18 mm Hg;  $n_D^{16}$  1.4359.

*c.* Preparation of methyl 1-methoxycyclopropanecarboxylate

A mixture containing 34.8 g (0.21 mole) methyl 4-chloro-2-methoxybutyrate, 150 cm<sup>3</sup> benzene and sodamide freshly prepared from 5.3 g (0.23 gram atom) sodium is heated under reflux for thirty-six hours. Sufficient water is added to the cold mixture to dissolve the water-soluble constituents, and the organic phase is separated, dried and filtered. To eliminate the unsaturated secondary products, the filtrate is caused to react with small portions of bromine dissolved in chloroform until the reaction stops, as indicated by the fact that the color of the bromine no longer disappears. After removing the benzene by distillation at atmospheric pressure, the residue is distilled to obtain 12 g colorless liquid product, boiling point 77-80°C under 43 mm Hg;  $n_D^{18}$  1.4294.

*d.* Preparation of 3',4'-dichloro-1-methoxycyclopropanecarboxamide

A slurry of 17.9g (0.138 mole) methyl 1-methoxycyclopropanecarboxylate, 22.4 g (0.138 mole) 3,4-dichloroaniline, 9.0 g (0.166 mole) sodium methoxide and 210 cm<sup>3</sup> benzene is agitated for twelve hours while slowly removing the benzene-methanol azeotrope. The mixture is cooled, and 50 cm<sup>3</sup> water and 15 cm<sup>3</sup> concentrated hydrochloric acid in 40 cm<sup>3</sup> water is added. The organic phase is separated, extracted with dilute hydrochloric acid then with water, dried and decolorized. After removing the benzene under reduced pressure, the residue is recrystallized from ligroin to obtain 25 g product, melting point 89-91°C.

The following example shows the activity of many of the compounds as post-germination herbicides at a rate of 5.6 kg/hectare.

*Example 18.* To prepare an aqueous suspension of the chemical agent, 0.4 g of the agent to be tested and 4 cm<sup>3</sup> of a solvent mixture (three parts Emulphor EL-719, one part benzene and one part kerosene) are combined, then sufficient hot water is added to make up 40 cm<sup>3</sup> mixture. "Emulphor EL-719" is the trademark of a polyoxyethyl vegetable oil.

In 10-cm pots in a greenhouse are planted oats, wheat, peas, radishes, flax, millet, lucerne, tomatoes and sugar beets. Then, ten-eighteen days after the emergence of the plants they are sprayed with the aqueous emulsions prepared as above, at a rate of 5.6 kg/hectare of active ingredient with a volume of 560 liters per hectare. Seven days after application, the plants are observed and the results of the treatment are indicated in Table III.

a b c d e f g h i j

TABLE III

Compound	Avoine	Froment	Soja	Radis	Lin	Millet	Lucerne	Tomate	Betterave sucrière
N-(3,4-dichlorophényl)-1-méthylcyclopropanecarboxamide.	N4	N4	N4 *	-	N4	N4	N4	N4	N4
N-(3-chlorophényl)-1-méthylcyclopropanecarboxamide.	N1G1	N4	N4 *	-	N4	N4	N4	N4	N4
N-phényl-1-chlorocyclopropanecarboxamide.....	O	G1	O	O	N2	N1	G1	O	G1
N-(3,4-dichlorophényl)-1-méthylcyclopropanecarboxamide.	N3	N2	C2 *	N4	N3	N4	N4	O	N4
N-phényl-1-phénylcyclopropanecarboxamide.....	O	O	O	O	O	O	O	O	O
N-(3-chlorophényl)-1-chlorocyclopropanecarboxamide.	G1	O	N1	N2	N3	O	N2	N1	N1
N-(3-chloro-4-méthylphényl)-1-chlorocyclopropanecarboxamide.	O	O	N1	N2	N1	N3	N2	N1	N3
N-(3-chloro-4-méthylphényl)-1-méthylcyclopropanecarboxamide.	N2	G2	N1	N3	N3	-	N4	N3	N4
N-(3,4-dichlorophényl)-1-butylcyclopropanecarboxamide.	O	O	N1	O	N1	O	-	N	O
N-(2,6-dichlorophényl)-méthyl-cyclopropanecarboxamide.	O	O	O	O	O	O	O	O	O
N-(2,6-diméthylphényl)-1-méthyl-cyclopropanecarboxamide.	O	O	O	O	O	O	O	O	O
N-(5-chloro-2-méthylphényl)-1-méthylcyclopropanecarboxamide.	C1	C1	C2	C3N1	G1	G2N2	N3C2	N2	N4
N-(3,4-dichlorophényl)-1-bromocyclobutane-carboxamide.	O	O	O *	N2	N2	N4	N2	O	N2
N-phényl-1-bromocyclobutanecarboxamide.....	O	O	O *	N2	N1	N4	N2	O	N1
1-(3,4-dichlorophényl)-1-méthoxycyclopropanecarboxamide.	N1G1	N1G1	N2		4	4	4	N3	4
N-(5-chloro-1-méthylphényl)-1-méthoxycyclopropanecarboxamide.	O	O	O		O	N2	O	O	O
N-(2,5-dichlorophényl)-1-méthoxycyclopropanecarboxamide.	O	O	O		O	O	O	O	O

\* Dans ces essais on utilise des pois.

k

## KEY TO TABLE III:

a. Compound; b. Oats; c. Wheat; d. Soybeans; e. Radishes; f. Flax; g. Millet; h. Lucerne; i. Tomatoes; j. Sugar beet  
k. \* Peas were used in these tests

TABLE IV

a	b	c	d	e	f	g	h	i	j	k	l	m
Composé	Lucerne	Brome	Lia	Avoine	Radis	Letternve sucrière	Mats	Coxcomb	Coton	Digitaria	Millet	Soja
N-(3,4-dichlorophényl)-1-méthyl- cyclopropanecarboxamide.	N4	N4	N4	N4	N4	N4	N3	N4	N2	N4	N4	N4
N-(3-chlorophényl)-1-méthyl- cyclopropanecarboxamide.	N4	N4	N3G4	N4	N3	N4	G2	N4	G2	N2	N4	C3K3
N-phényl-1-chlorocyclopropane- carboxamide.	O	O	O	O	O	O	O	O	O	O	O	O
N-(3,4-dichlorophényl)-1-méthyl- cyclopropanecarboxamide.	N4	N3	N2	N2	N4	N4	O	N4	O	N4	N4	C2K2 C3
N-phényl-1-phénylcyclopropane- carboxamide.	O	O	O	O	O	O	O	O	O	O	O	O
N-(3-chlorophényl)-1-chlorocyclo- propanecarboxamide.	N4	K4	G2	G2	O	O	K2G2	N4	G2	N2G2	N3G2	K4
N-(3-chloro-4-méthyl)-phényl-1- chlorocyclopropanecarboxamide.	N3	O	O	O	O	O	G1	N4	O	N2G2	N3G2	K4
N-(3-chloro-4-méthyl)-phényl-1- méthylcyclopropanecarboxamide.	N3	N1	N2K2	O	O	N2	O	N4	O	O	O	O
N-(3,4-dichlorophényl)-1-butyl- cyclopropanecarboxamide.	O	O	O	O	O	O	O	O	O	O	O	O
N-(2,6-dichlorophényl)-1-mé- thylcyclopropanecarboxamide.	G2	N4	N1	K3N1	G2	N1	N1	O	O	N2	N3	N2
N-(2,6-diméthylphényl)-1-méthyl- cyclopropanecarboxamide.	N4	N1	N1	N1	N1	N1	N1	N2	O	N2	N3	N1
N-(5-chloro-2-méthylphényl)-1- méthylcyclopropanecarboxamide.	N4	N4	N4	N4	N4	N4	C4	N4	O	C4	C4	C4
N-(3,4-dichlorophényl)-1-bromo- cyclobutanecarboxamide.	N4	O	N2	O	O	O	O	N4	O	O	N4	C2
N-phényl-1-bromocyclobutanecar- boxamide.	O	O	O	O	O	K2	O	O	O	O	O	O
N-(3,4-dichlorophényl)-1-métho- xy-cyclopropanecarboxamide.	N4	N4	N4	N3	N4	N4	N4	N4	G2	N4	N4	G1C2
N-(chloro-2-méthylphényl)-1-mé- thoxy-cyclopropanecarboxamide	N4	N3	N4	N2	N4	N4	O	N4	N4	N4	N4	C3
N-(2,5-dichlorophényl)-1-métho- xy-cyclopropanecarboxamide.	O	O	O	O	O	O	O	O	O	N2	O	O

KEY TO TABLE IV:

a. Compound; b. Lucerne; c. Bromegrass; d. Flax; e. Oats; f. Radishes; g. Sugar beets; h. Corn; i. Coxcomb; j. Cotton; k. Digitaria; l. Millet; m. Soybeans

The notes shown are as follows:

C = chlorosis  
 N = necrosis  
 G = inhibition of growth  
 K = no germination  
 F = effect on development  
 0 = no effect  
 1 = slight effect  
 2 = moderate effect  
 3 = pronounced effect  
 4 = maximum effect or plants dead.

(See Table III page 4)

Disposable paper trays are sown and the solutions in acetone are sprayed on to them at a rate of 5.6 kg active ingredient per hectare. A tray sown with lucerne, brome grass, flax, oats, radishes and sugar beets is kept at 24°C. Another tray sown with corn, coxcomb, cotton, digitaria, millet and soybeans is kept at 29°C. The trays are examined twenty-one days after the sowing and the treatment, the germination of the plants and the effects of the chemical agent on the young shoots are evaluated, and the notes are indicated on Table IV. The same system of notation is used as in example 18.

(See Table IV, page 5.)

The following example illustrates the activity of many invention compounds as pre-emergent herbicides at a rate of 11.2 kg/hectare.

*Example 19.* A solution of the chemical agent to be tested is prepared by dissolving 290 mg of the latter in 200 cm<sup>3</sup> acetone.

*Example 20.* N-(2-methyl-5-chlorophenyl)-1-methylcyclopropanecarboxamide is tested as a pre-emergent herbicide by the method in Example 19, but with the dosages 5.6, 2.24, and 1.12 kg/hectare. The results are indicated in table V:

g      h

a      b      c      d      e      f      TABLE V      i      j      k      l      m

Dose	Lucerne	Brome	Lin	Avoine	Radis	Bette- rave su- crière	Maïs	Cox- comb	Coton	Digitaria	Millet	Soja
kg/ha												
5,6.....	N4	N4	N4	C3G2	N4	N4	C4	N4	0	N4	N4	C3
2,24.....	N4	N4	C3	C2	C4	N4	C3	N4	0	C3	N4	C2
1,12.....	N4	C3	C1	C1	C4	N4	C2	N3	0	C4	C4	C2

**KEY TO TABLE V:**

a. Dosage      b. Lucerne      c. Brome grass      d. Flax      e. Oats      f. Radishes  
 g. Sugar beets      h. Corn      i. Coxcomb      j. Cotton      k. Digitaria      l. Millet      m. Soybeans

These data indicate that N-(2-methyl-5-chlorophenyl)-1-methylcyclopropanecarboxamide is an excellent pre-emergent herbicide for certain plants such as lucerne, brome grass, coxcomb, and in particular digitaria, at ranges as low as 1.12 kg/hectare.

In formula (I), R<sub>1</sub> is preferably an alkyl or haloalkyl group with 1-8 carbon atoms, a monocyclic aryl group, for example phenyl, tolyl, xylyl, etc., and a halogen atom, that is, fluorine, chlorine, bromine or iodine; in a more particularly preferred class of compounds, R<sub>2</sub> is a hydrogen atom and R<sub>3</sub> is a monocyclic aryl group, for example a phenyl group, possibly substituted; in the particular case where R<sub>2</sub> is a monocyclic aryl group, R<sub>3</sub> can be a hydroxy group.

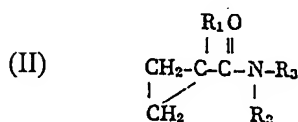
Examples of the substituents R<sub>2</sub> and R<sub>3</sub> in the above formula that may be cited are alkyl groups, especially the

lower alkyl groups containing about 1-8 carbon atoms, with straight or branched chains; cycloalkyl groups, especially the lower cycloalkyl groups with about 3-8 carbon atoms; alkenyl and alkynyl groups, especially lower ones containing about 2-8 carbon atoms; aralkyl groups, especially monocyclic groups such as benzyl groups, possibly substituted on the nucleus; aryl groups, especially monocyclic aryl groups such as phenyl and phenyl groups having on the nucleus substituents such as halogens (chlorine, iodine, fluorine, bromine), alkoxy groups, especially lower alkoxy groups containing 1-8 carbon atoms, cyanogenic groups, nitro, alkyl group, especially lower alkyl groups containing 1-8 carbon atoms, acyloxy or hydroxy groups; heterocyclic groups, especially monocyclic groups containing in the ring at least one atom of nitrogen, oxygen or sulfur (or two or more heteroatoms) in addition to the carbon atoms. R<sub>2</sub> and R<sub>3</sub> can also be linked together and form with one

nitrogen of the amide group a heterocyclic radical, for example a monocyclic radical containing in the ring atoms of nitrogen, oxygen or sulfur as well as carbon atoms, as in the case of amides derived from piperidine, piperazine, morpholine, etc.

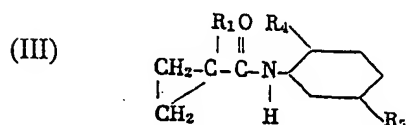
Examples of radicals represented by  $R_2$  and  $R_3$  in the above formula that may be cited are: hydrogen and methyl, ethyl, 2-chloroethyl, 2-hydroxyethyl, propyl, isobutyl, pentyl, isooctyl, allyl, butenyl, pentenyl, butynyl, 4-chloro-2-butenyl, propynyl, phenyl, naphthyl, 3-chlorophenyl, 3-iodophenyl, 3-fluorophenyl, 4-bromophenyl, 3,4-dichlorophenyl, 2,4,5-trichlorophenyl, 3-methylphenyl, 3,4-dibromophenyl, 2,5-difluorophenyl, 4-cyanophenyl, 3,5-dinitrophenyl, 4-hydroxyphenyl, 3-chloro-4-methylphenyl, 4-acetoxyphenyl, 3-methoxyphenyl, 3-trifluoromethylphenyl, cyclopropyl, cyclohexyl, cyclobutyl, 4-cyclopropylcarbonyloxyphenyl, benzyl, 3,4-dichlorobenzyl, thiazolyl-2, pyridyl-2 and triazolyl groups. The compounds containing a cyclic radical in which the hydrogen atom of the amide group is part of the ring are formed starting from compounds such as piperidine, morpholine and pyrrolidine.

A preferred sub-group of the invention compounds corresponds to the formula:



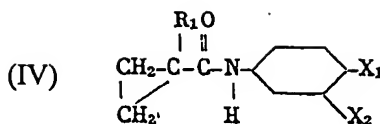
in which  $R_1$ ,  $R_2$ , and  $R_3$  correspond to the definition already given.

Another more limited group of compounds that constitute a particularly preferred form of execution of the invention correspond to the formula:



in which  $R_1$  corresponds to the above definition,  $R_4$  is an alkyl group with 1-8 carbon atoms (especially a methyl group), and  $R_5$  is an alkyl group with 1-8 carbon atoms or a halogen atom, in particular chlorine. Particularly preferred compounds, especially from the economic viewpoint, are those in which  $R_4$  is a methyl group and  $R_5$  is a chlorine atom, a methyl group or an isopropyl group.

Another group of particularly preferred compounds correspond to the formula:



In which  $R_1$  corresponds to the definition already given, and  $X_1$  and  $X_2$  represent, independently, atoms of hydrogen, fluorine or chlorine, or methyl groups, at least one of these two substituents being an atom of chlorine or fluorine.

The cycloalkanecarboxamides of the invention can be easily prepared by causing cycloalkanecarbonyl halides such as the chlorides to react with an appropriate amine. Preferably, the reaction is carried out in the presence of an inert organic solvent such as cyclohexane, toluene, dioxan, benzene, n-hexane or n-pentane. Given that halohydric acid is a secondary product of the reaction, it is desirable to use a molar excess of the amine or preferably a tertiary amine such as triethylamine or pyridine to react with the halohydric acid liberated, which improves the yield and purity of the desired product. This reaction progresses regularly at or slightly below ambient temperature, and normally it is finished in about 0.5-2 hours. The preferred temperature is about 15-25°C, which is low enough to permit good control of the reaction. To make best use of the reactants, it is preferable to add the acyl halide to a solution of the amine (and possibly of the tertiary amines used as acceptors) in an organic solvent so as to maintain an excess of amine for the duration of the reaction. When an organic solvent is used that dissolves the cycloalkanecarboxamide, the pyridine hydrohalide formed as a secondary product can be eliminated by filtration and the desired cycloalkanecarboxamide can be isolated from the solvent by known methods. The crude amine can be recrystallized from solvents such as a mixture of water and alcohol, n-hexane or ethyl acetate. When the reaction product is a liquid, it can be purified by distillation under reduced pressure.

In a preferred variant of the procedure, the cycloalkanecarboxamides can be prepared by causing an appropriate cycloalkanecarboxylic acid ester to react with the appropriate amine in the presence of an equimolar quantity of an alkali alcoholate.

To prepare the thio analogs of the cycloalkanecarboxamides ( $X$  in Formula I being a sulfur atom), the oxygenated analogs can be caused to react with phosphorus pentasulfide at elevated temperature, for example about 90-110°C.

The cycloalkanecarboxamides of the invention can be used as herbicides at a rate of 0.1-22.4 kg/hectare. When the compounds are used as pre-emergent herbicides, a dosage of about 0.56-22.04 kg/hectare is normally

applied, preferably about 2.24-11.2 kg/hectare. When they are used as post-emergent herbicides, a dosage of about 0.01-22.4 kg/hectare of one or more active components is used, preferably 0.1-3.36 kg/hectare. When an aqueous emulsion of the herbicide is used, a spray volume of about 9.35-935 liters of aqueous emulsion is used, preferably about 46.8-374 liters per hectare.

The invention cycloalkanecarboxamides display good activity against several species of plants. With regard to a number of closely related species, they also display better selectivity than the usual compounds that have such an elevated degree of activity. The selectivity of the destruction can be reinforced by using appropriate mixtures and dosages.

The cycloalkanecarboxamides have high resistance to the majority of the common microorganisms in the soil, and when they are used before germination they give significant destruction over a prolonged period of time.

Certain types of 1-substituted cycloalkanecarboxamides substituted at 1, particularly N-(2-methyl-5-chlorophenyl)-1-methylcyclopropanecarboxamide, appear to have a remarkable activity as pre-germination herbicides against digitaria in grassy meadows.

The excellent herbicidal activity of the invention cycloalkanecarboxamides requires the application of only small quantities of the active ingredient, uniformly distributed over a large area. Of course, this is difficult when the pure material is used. However, by increasing the mass of material, for example by mixing the compound with a diluent or inert vehicle, the application to plants in the course of growth and to the soil can be more easily effectuated. The vehicles can be solids such as talc, clay, infusorial earth, sawdust, calcium carbonate, etc., or also liquids such as water, kerosene, acetone, benzene, toluene, xylene, etc., in which the active compound can be dissolved or dispersed.

Emulsifiers are preferably used to obtain an appropriate emulsion or dispersion in liquids such as water, so as to effectuate spraying. Emulsifiers and wetting agents can also be used to facilitate the dispersion of the active compound in the liquids used as vehicles in which the compound is not completely soluble, and to increase the dissemination of the active compound. Emulsifiers and wetting agents, also called surfactants, are sold under many trade names and can be either pure compounds or mixtures of compounds of the same general group or even mixtures of compounds of different classes.

Thus, the invention permits the preparation of new herbicidal compositions containing one or several of the above cycloalkanecarboxamides, intimately dispersed or dissolved in a surfactant. Types of surfactants that can be used are the higher alkali alkylarenesulfonates such as sodium dodecylbenzenesulfonate and the sodium salts of the alkylnaphthalenesulfonic acids, sulfates of fatty acids such as the sodium salts of the monoesters formed by sulfuric acid with normal aliphatic alcohols containing about 8-18 carbon atoms, long-chain quaternary ammonium compounds, sodium salts of alkanesulfonic acids derived from petroleum, polyethylene sorbitan monooleate, alkylaryl polyether-alcohols, water-soluble lignin sulfonate salts, alkali-casein compositions, long-chain alcohols usually containing about 10-18 carbon atoms, and the products of the condensation of ethylene oxide with fatty acids, alkylphenols or mercaptans.

Other additives such as an emulsion of lanolin or kerosene or "Tween 20" (trade name of a polyoxyalkylene derivative of sorbitan monolaurate), adhesives and other adjuvants can be included in the solid or liquid compositions to increase the dissemination of the active compound. These materials are also considered like surfactants.

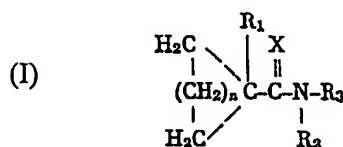
The above description, and in particular the examples, serve only as illustration and one skilled in the art could provide modifications without in any way departing from the scope of the invention.

## SUMMARY

The invention has as its subject:

I. Cycloalkanecarboxamides characterized by the following points, taken in isolation or in various combinations:

1. They correspond to the formula:



in which:

n is 0 or 1;

R<sub>1</sub> is an alkyl, haloalkyl, alkoxy, or aryl group or a halogen atom;

R<sub>2</sub> and R<sub>3</sub> are, independently, hydrogen atoms or alkyl, cycloalkyl, alkenyl, alkynyl, aryl, alkaryl, haloaryl, haloalkaryl or aralkyl groups or heterocyclic groups, but



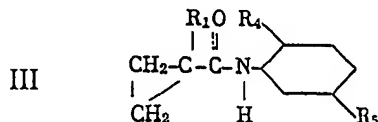
can also together form a heterocyclic radical with the nitrogen atom to which they are attached;

X is an atom of oxygen or sulfur.

2.  $R_2$  is hydrogen and  $R_3$  is a monocyclic aryl group.

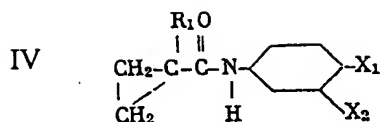
3.  $R_2$  is a hydroxyl group and  $R_3$  is a monocyclic aryl group.

4. They correspond to the formula:



in which  $R_4$  is an alkyl group with 1-8 carbon atoms and  $R_5$  is an alkyl group with 1-8 carbon atoms, or a halogen atom.

5. They correspond to the formula:



in which

$X_1$  and  $X_2$  independently represent hydrogen, fluorine or chlorine atoms or methyl groups, at least one of these two substituents being a chlorine or fluorine atom.

II. Herbicidal compositions containing a surfactant and a compound as in I.

III. A procedure aiming to prevent the growth of plants which consists of applying a composition as in II.

CHEMICAL INVESTORS, S.A.

By proxy:

BEAU DE LOMENIE, Andre ARMENGAUD  
& G. HOUSSARD

18624

Nouveaux composés chimiques et composition herbicide contenant ceux-ci.

Société dite : CHEMICAL INVESTORS S. A. résidant dans le Grand-Duché de Luxembourg.

Demandé le 23 mars 1964, à 13<sup>h</sup> 56<sup>m</sup>, à Paris.

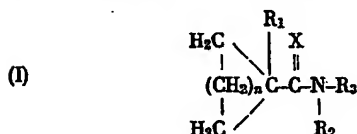
Délivré par arrêté du 12 avril 1965.

(Bulletin officiel de la Propriété industrielle, n° 21 de 1965.)

(2 demandes de brevets déposées aux États-Unis d'Amérique les 28 mars 1963, sous le n° 268.581, au nom de M. Thomas, Robert HOPKINS et 8 mai 1963, sous le n° 278.974, au nom de M. Kenneth, Paul DUBROVIN.)

L'invention a pour objet de nouveaux composés chimiques, des compositions herbicides contenant ceux-ci comme ingrédient actif et des procédés visant à empêcher la croissance des plantes à l'aide de ces compositions.

Les nouveaux composés chimiques suivant l'invention répondent à la formule :



dans laquelle :

$n$  vaut 0 ou 1;

$\text{R}_1$  est un groupe alkyle halogénoalkyle, alcoyle, aryle ou un atome d'halogène;

$\text{R}_2$  et  $\text{R}_3$  sont, indépendamment, des atomes d'hydrogène ou des groupes alkyle, cycloalkyle, alcényle, alcynyle, aralkyle, aryle, alcaryle, halogénoaryle, halogénoalcaryle ou des groupes hétérocycliques, mais peuvent aussi former ensemble un radical hétérocyclique avec l'atome d'azote auquel ils sont rattachés;  $\text{X}$  est un atome d'oxygène ou de soufre.

Pour simplifier la description, ces composés seront appelés ci-après « cycloalcanecarboxamides ». Comme on le voit, les composés de l'invention sont ou bien des amides non substituées, ou bien des amides portant un ou plusieurs substituants organiques sur l'atome d'azote.

Les cycloalcanecarboxamides ci-dessus peuvent être mélangées à des véhicules inertes, émulsifiants, etc., pour former des compositions herbicides qui peuvent servir efficacement à empêcher la croissance des plantes. Les compositions herbicides obtenues peuvent servir avant ou après la sortie de terre.

Les exemples suivants sont donnés pour illustrer

plus clairement le principe et la pratique de l'invention.

Exemples 1 à 4. — Pour préparer quatre amides d'acide 1-méthylcyclopropanecarboxylique, on fait réagir le 1-méthylcyclopropanecarboxylate de méthyle respectivement sur la 3-chloraniline, la 3-chloro-4-méthylaniline, la 2-méthyl-5-chloraniline et la 3,4-dichloraniline.

Dans chaque synthèse, on agite 0,1 mole de 1-méthylcyclopropanecarboxylate de méthyle, 0,1 mole de l'amine, 0,11 mole de méthoxyde de sodium et 200 cm<sup>3</sup> de benzène et on chauffe au reflux doux. On continue le reflux pendant environ douze heures tout en éliminant l'azéotrope benzène-méthanol à mesure qu'il se forme. On refroidit le mélange réactionnel à la température ambiante puis on y ajoute 50 cm<sup>3</sup> d'eau et 15 cm<sup>3</sup> d'acide chlorhydrique concentré dissous dans 40 cm<sup>3</sup> d'eau. Après avoir bien mélangé, on récupère la phase organique par décantation et on l'extrait successivement par l'acide chlorhydrique dilué et par l'eau. On sèche la phase organique et on la décolore sur du charbon. Après avoir éliminé le benzène sous pression réduite, on recristallise par la ligroïne les amides obtenues. L'identification des amides préparées (exemples 1, 2, 3 et 4) et leurs points de fusion sont indiqués au tableau I.

On prépare de préférence trois amides d'acide 1-méthylcyclopropanecarboxylique par une variante dans laquelle on fait réagir le chlorure de 1-méthylcyclopropanecarbonyle respectivement sur la 2,6-dichloraniline, la 2,6-diméthylaniline et la 2,5-diméthylaniline. On prépare avantageusement le chlorure d'acyle en faisant réagir au repos pendant environ seize heures une solution de 7,8 g (0,078 mole) d'acide 1-méthylcyclopropanecarboxylique sur 20 cm<sup>3</sup> de chlorure de thionyle, puis en éliminant l'excès de chlorure de thionyle par distillation sous pression réduite. Le résidu est essentiel-

TABLEAU II

Exemple	Amide	Point de fusion °C
VIII.....	N-p-(phénylazo) phényl-1-chloro- cyclopropanecarboxamide.	196-198
IX.....	N-(p-acétylphényl)-1-chlorocyclo- propanecarboxamide.	183-185
X.....	N-phényl-1-chlorocyclopropane- carboxamide.	62-63
XI.....	N-(3,4-chlorophényl)-1-chlorocyclo- propanecarboxamide.	95-96
XII.....	N-(3-chlorophényl)-1-chlorocyclo- propanecarboxamide.	73-74
XIII.....	N-(3-chloro-4-méthylphényl)-1- chloro cyclopropanecarboxamide.	89-90

pour obtenir la N-(3,4-dichlorophényl)-1-bromocyclobutanecarboxamide qui fond à 96-97 °C.

*Exemple 15.* — On prépare la N-phényl-1-bromocyclobutanecarboxamide en faisant réagir le chlorure de 1-bromocyclobutanecarboxyle sur l'aniline par le procédé décrit à l'exemple 14. Le composé fond à 89-90 °C.

*Exemple 16.* — On prépare la N-phényl-1-phénylcyclopropanecarboxamide en faisant réagir le chlorure de 1-phénylcyclopropane carboxyle sur l'aniline par le procédé de l'exemple 14. Le composé fond à 123-125 °C.

*Exemple 17.* — a. Préparation du 4-chloro-2-méthoxybutyronitrile.

On prépare ce composé par un procédé similaire à celui qui est utilisé par Wilson et Henze, *J. Am. Chem. Soc.* 63, 2112 (1941), pour préparer le 4-chloro-1-éthoxy-butyrionitrile.

A 147 g (1,1 mole) de cyanure d'argent dispersé dans 300 cm<sup>3</sup> d'éther anhydre, on ajoute une solution de 140 g (0,98 mole) de 1,3-dichloro-1-méthoxypropane dans 250 cm<sup>3</sup> d'éther anhydre. Il se produit un reflux doux pendant l'addition. Une fois l'addition achevée, on agite la bouillie pendant une nuit à la température ambiante. On filtre alors le mélange et on chasse l'éther par distillation. On distille alors le résidu pour obtenir 78,1 g, le produit bouillant à 67-69 °C sous une pression de 8 mm de Hg;  $n_D^{17}$  1,4339.

b. Préparation du 4-chloro-2-méthoxybutyrate de méthyle.

On prend une solution de 40 g (0,3 mole) de 4-chloro-2-méthoxybutyronitrile dans 80 cm<sup>3</sup> de méthanol, on la sature d'acide chlorhydrique à la température ambiante puis on chauffe au reflux pendant seize heures. On verse le mélange dans 150 cm<sup>3</sup> d'eau froide, on sépare la couche organique et on extrait la couche aqueuse par trois petites portions d'éther pour récupérer un supplément de produit de la phase aqueuse. On réunit les phases

organiques, on les sèche puis on les distille pour obtenir 37 g de produit bouillant à 93-96 °C sous 18 mm de Hg;  $n_D^{16}$  1,4359.

c. Préparation du 1-méthoxycyclopropanecarboxylate de méthyle.

On chauffe au reflux pendant trente-six heures un mélange comprenant 34,8 g (0,21 mole) de 4-chloro-2-méthoxybutyrate de méthyle, 150 cm<sup>3</sup> de benzène et de l'amidure de sodium fraîchement préparé à partir de 5,3 (0,23 atome-gramme) de sodium. On ajoute suffisamment d'eau au mélange froid pour dissoudre les constituants hydrosolubles et on sépare la phase organique on la sèche et on la filtre. Pour éliminer les sous-produits non saturés, on fait réagir le filtrat sur de petites portions de brome dissous dans du chloroforme jusqu'à ce que la réaction cesse, comme l'indique le fait que la couleur du brome ne disparaît plus. Après avoir chassé le benzène par distillation à la pression atmosphérique, on distille le résidu pour obtenir 12 g de produit liquide incolore, point d'ébullition 77-80 °C sous 43 mm de Hg;  $n_D^{18}$  1,4294.

d. Préparation de la 3',4'-dichloro-1-méthoxycyclopropanecarboxamide.

On agite pendant douze heures une bouillie de 17,9 g (0,138 mole) de 1-méthoxycyclopropanecarboxylate de méthyle, 22,4 g (0,138 mole) de 3,4-dichloraniline, 9,0 g (0,166 mole) de méthoxyde de sodium et 210 cm<sup>3</sup> de benzène tout en chassant lentement l'azéotrope benzène-méthanol. On refroidit le mélange, puis on ajoute 50 cm<sup>3</sup> d'eau et 15 cm<sup>3</sup> d'acide chlorhydrique concentré dans 40 cm<sup>3</sup> d'eau. On sépare la phase organique on l'extrait par l'acide chlorhydrique dilué puis par l'eau, puis on sèche et on décolore. Après avoir éliminé le benzène sous pression réduite, on recristallise le résidu par la ligroïne pour obtenir 25 g de produit, point de fusion 89-91 °C.

L'exemple suivant montre l'activité de beaucoup des composés comme herbicides après la germination, à raison de 5,6 kg/ha.

*Exemple 18.* — Pour préparer une suspension aqueuse de l'agent chimique, on réunit 0,4 g de l'agent à essayer et 4 cm<sup>3</sup> d'un mélange solvant (trois parties d'Emulphor EL-719, une partie de benzène et une partie de pétrole lampant) puis on ajoute suffisamment d'eau chaude, pour faire 40 cm<sup>3</sup> de mélange. L'« Emulphor EL-719 » est une marque commerciale d'huile végétale polyoxyéthyle.

On plante dans des pots de 10 cm, en serre, de l'avoine, du froment, des pois, des radis, du lin, du millet, de la luzerne, des tomates et des betteraves sucrières. Puis, dix-dix-huit jours après la sortie des plantes, on y pulvérise les émulsions aqueuses préparées comme ci-dessus, à raison de 5,6 kg/ha d'ingrédient actif avec un volume de 560 litres par hectare. Sept jours après l'applica-

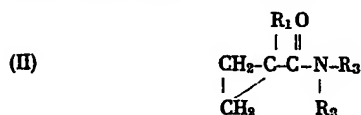
TABLEAU IV

[illegible]

atomes de carbone, comme dans le cas des amides dérivées de la pipéridine, de la pipérazine de la morpholine, etc.

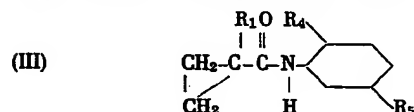
Comme exemples de radicaux représentés par  $R_2$  et  $R_3$  dans la formule ci-dessus, on citera l'hydrogène et les groupes méthyle, éthyle, 2-chloréthyle, 2-hydroxyéthyle, propyle, isobutyle, pentyle, iso-octyle, allyle, butényle, pentényle, butynyle, 4-chloro-2-butynyle, propynyle, phényle, naphthyle, 3-chlorophényle, 3-iodophényle, 3-fluorophényle, 4-bromophényle, 3,4-dichlorophényle, 2,4,5-trichlorophényle, 3-méthylphényle, 3,4-dibromophényle, 2,5-difluorophényle, 4-cyanophényle, 3,5-dinitrophényle, 4-hydroxyphényle, 3-chloro-4-méthylphényle, 4-acétoxyphényle, 3-méthoxyphényle, 3-trifluorométhylphényle, cyclopropyle, cyclohexyle, cyclobutyle, 4-cyclopropylcarbonyloxyphényle, benzyle, 3,4-dichlorobenzyle, thiazolyle-2, pyridyle-2 et triazolyle. Les composés contenant un radical cyclique dans lequel l'atome d'hydrogène du groupement amide fait partie du noyau sont formés à partir de composés tels que la pipéridine, la morpholine et la pyrrolidine.

Un sous-groupe préférentiel de composés de l'invention répondent à la formule :



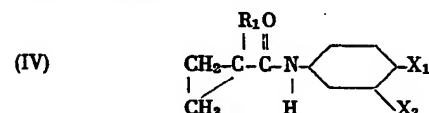
dans laquelle  $R_1$ ,  $R_2$  et  $R_3$  répondent à la définition déjà donnée.

Un autre groupe plus limité de composés, qui constituent une forme de réalisation spécialement préférentielle de l'invention, répondent à la formule :



dans laquelle  $R_1$  répond à la définition ci-dessus,  $R_4$  est un groupe alkyle à 1-8 atomes de carbone (spécialement un groupe méthyle) et  $R_5$  est un groupe alkyle à 1-8 atomes de carbone ou un atome d'halogène, spécialement de chlore. Les composés particulièrement préférentiels, notamment du point de vue économique, sont ceux dans lesquels  $R_4$  est un groupe méthyle et  $R_5$  est un atome de chlore, un groupe méthyle ou un groupe isopropyle;

Un autre groupe de composés spécialement préférentiels répondent à la formule :



dans laquelle  $R_1$  répond à la définition déjà donnée, et  $X_1$  et  $X_2$  représentent, indépendamment, des

atomes d'hydrogène, de fluor ou de chlore ou des groupes méthyle, au moins un de ces deux substituants étant un atome de chlore ou de fluor.

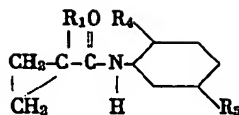
On peut facilement préparer les cycloalcanecarboxamides de l'invention en faisant réagir des halogénures de cycloalcanecarbonyle tels que les chlorures sur une amine appropriée. De préférence, on conduit la réaction en présence d'un solvant organique inerte tel que le cyclohexane, le toluène, le dioxane, le benzène, l'hexane-n ou le pentane-n. Étant donné que l'acide halogénhydrique est un sous-produit de la réaction, il est désirable d'utiliser un excès molaire de l'amine ou de préférence une amine tertiaire comme la triéthylamine ou la pyridine pour réagir sur l'acide halogénhydrique libéré, ce qui améliore le rendement et la pureté du produit désiré. Cette réaction se déroule régulièrement à la température ambiante ou légèrement en dessous et normalement, elle est terminée en 0,5-2 heures environ. La température préférentielle est d'environ 15-25 °, ce qui est suffisamment bas pour permettre de bien maîtriser la réaction. Pour tirer pleinement parti des réactifs, il est préférable d'ajouter l'halogénure d'acyle à une solution de l'amine (et éventuellement des amines tertiaires utilisées comme accepteurs) dans un solvant organique, de manière à maintenir un excès de l'amine pendant la durée de la réaction. Quand on utilise un solvant organique qui dissout la cycloalcanecarboxamide, on peut éliminer par filtration l'halogénhydrate de pyridine formé comme sous-produit on peut isoler du solvant la cycloalcanecarboxamide désirée, par des procédés connus. On peut recristalliser l'amine brute par des solvants tels qu'un mélange d'eau et d'alcool, l'hexane-n ou l'acétate d'éthyle. Quand le produit réactionnel est un liquide, on peut le purifier par distillation sous pression réduite.

Dans une variante préférentielle du procédé, on peut préparer les cycloalcanecarboxamides en faisant réagir un ester d'acide cycloalcanecarboxylique approprié sur l'amine appropriée en présence d'une quantité équimolaire d'un alcoolate alcalin.

Pour préparer les thioalogues des cycloalcanecarboxamides (X de la formule I étant un atome de soufre), on peut faire réagir les analogues oxygénés sur le pentasulfure de phosphore à température élevée, par exemple à 90-110 °C environ.

Les cycloalcanecarboxamides de l'invention peuvent être utilisées comme herbicides à raison de 0,1-22,4 kg/ha. Quand on utilise les composés comme herbicides avant germination, on applique normalement une dose d'environ 0,56-22,04 kg/ha, de préférence environ 2,24-11,2 kg/ha. Quand on les utilise comme herbicides après germination, on utilise une dose d'environ 0,01-22,4 kg/ha d'un ou plusieurs composés actifs, de préférence 0,1-3,36 kg/ha. Quand on utilise une émulsion aqueuse de l'herbi-

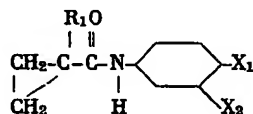
(III)



dans laquelle R<sub>4</sub> est un groupe alkyle de 1-8 atomes de carbone et R<sub>5</sub> est un groupe alkyle de 1-8 atomes de carbone ou bien un atome d'halogène.

5° Elles répondent à la formule :

(IV)



dans laquelle X<sub>1</sub> et X<sub>2</sub> représentent indépendamment des atomes d'hydrogène, de fluor ou de chlore ou des groupes méthyle, au moins un de ces deux substituants étant un atome de chlore ou de fluor.

II. Des compositions herbicides comprenant un surfactif et un composé suivant I.

III. Un procédé visant à empêcher la croissance des plantes, qui consiste à appliquer une composition suivant II.

Société dite : CHEMICAL INVESTORS, S. A.

Par procuration :

BEAU DE LOMÉNIE, André ARMENGAUD & G. HOUSSARD